PREVENTION AND SAFE MANAGEMENT OF HYDRATES AND ICE IN PROCESS EQUIPMENT

Guideline (Draft)

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Setting the standard in oil and gas safety

ENDORSEMENT

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- Canadian Association of Geophysical Contractors (CAGC)
- Canadian Association of Oilwell Drilling Contractors (CAODC)
- Canadian Association of Petroleum Producers (CAPP)
- Canadian Energy Pipeline Association (CEPA)
- Explorers and Producers Association of Canada (EPAC)
- Petroleum Services Association of Canada (PSAC)

ABOUT ENERGY SAFETY CANADA

Energy Safety Canada is the oil and gas industry's advocate and leading resource for the continuous improvement of safety performance. Our mission is to help companies achieve their safety goals by providing practices, assessment, training, support, metrics and communication.

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This document is based on the Canadian Association of Petroleum Producers (CAPP) Prevention and Safe Handling of Hydrates Guide.

DISCLAIMER

This document is intended to be flexible in application and provide guidance to users rather than act as a prescriptive solution. Recognizing that one solution is not appropriate for all users and situations, it presents generally accepted guidelines that apply to industry situations, as well as recommended practices that may suit a company's particular needs. While we believe that the information contained herein is reliable under the conditions and subject to the limitations set out, Energy Safety Canada does not guarantee its accuracy. The use of this document or any information contained will be at the user's sole risk, regardless of any fault or negligence of Energy Safety Canada and the participating industry associations.

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1.0 INTRODUCTION

Hydrates are a mixture of water and gas molecules that crystallize to form a solid “ice plug” under appropriate conditions of temperature and pressure. Ice from frozen water is not strictly a hydrate but, for the purposes of prevention and mitigation, ice and hydrates are the same; therefore, when this guideline references hydrates it shall be taken to mean both hydrates and ice.

Hydrates can interrupt the flow of gas and liquids through wells, pipelines and operating equipment and, therefore, require prevention and safe handling when they occur. In the absence of adequate prevention and safe handling, hydrates can result in spills, damage to equipment, the release of large amounts of hazardous energy, and subsequent injury to personnel.

A review of available regulatory reports on process safety incidents in Western Canada, 14% of incidents involved hydrates or ice. For more information on this analysis please refer to Appendix I.

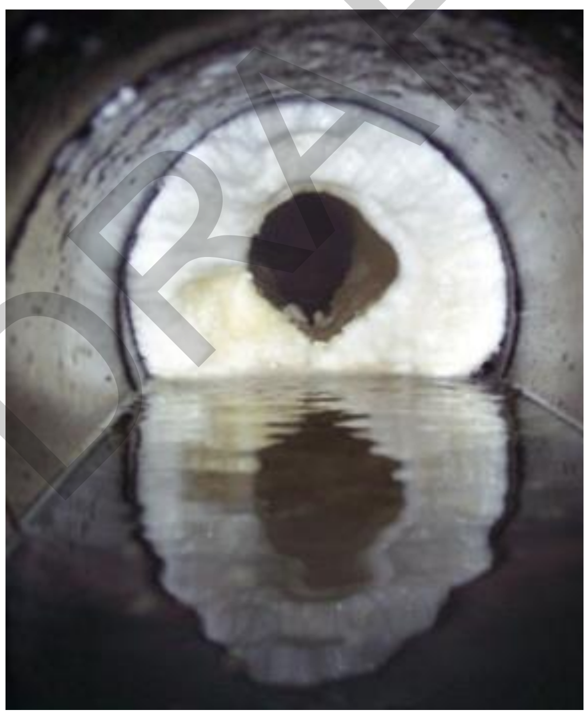

Figure 1. Photograph of a Hydrate within a Pipeline

2.0 REGULATIONS AND OTHER PRACTICES

There are no regulations specific to hydrates. Under Alberta regulations there is a requirement to identify known safety hazards and manage hazardous energy. Other jurisdictions have similar requirements.

Hydrates are referenced in the Industry Recommended Practice (IRP) #4 Well Testing and Fluid Handling within Appendix D produced by the Drilling and Completions Committee (DACC).

3.0 NATURE OF HYDRATES

Hydrates are a mixture of water and gas molecules that crystallize to form a solid "ice plug" under appropriate conditions of temperature and pressure. Hydrates can form from free water condensed in the gas stream at or below its water dew point. Hydrate formation will not occur if any one of the three required elements symbolized below are altered.

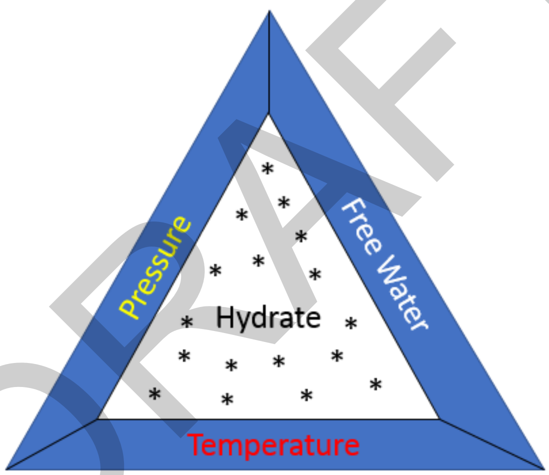

Figure 2. Hydrate Triangle

Hydrates can form in any segment of an operating system, such as:

- Downhole in wells
- Gathering systems
- Facility piping and equipment
- Well drilling and servicing equipment

An unusual characteristic of hydrates is that their formation is not strictly temperature dependent. They form at high pressure when the temperature of the flowing gas is well above the freezing point of water. Some locations where hydrates occur are where flow restrictions or reductions exist, such as at valves, changes in piping diameter, basket strainers, flow meters, etc.

Because hydrates restrict the normal flow of gas, a pressure drop across the hydrate will cause the gas to expand. This expansion cools the gas through auto-refrigeration, contributing to further growth of hydrates until normal flow is completely blocked.

No analytical methods can accurately predict whether hydrate formation will result in single or multiple plugs in any given situation. The formation of multiple hydrate plugs causes pressure to be trapped between the plugs. High differential pressures can be created if multiple hydrates are treated as a single plug. That is, high pressure can be trapped between the plugs even though the ends of the piping have been depressured. Once formed, hydrates pose a threat to people and equipment if not handled properly. The real hazard from hydrates comes in trying to remove them. Proper procedures can prevent pipe and vessel ruptures as well as personal injury. Refer to Section 7.0.

Key Concept: Always assume there are multiple hydrates and stored pressure between them

4.0 HOW HYDRATES ARE FORMED

Water is a loosely-formed group of molecules with spaces in between. When the spaces are filled with other molecules, such as hydrocarbon gases like [methane (C_1), ethane (C_2), propane (C_3), and butane (n-C_4 and i-C_4)] and/or impurities [nitrogen (N_2), carbon dioxide (CO_2) and hydrogen sulphide (H_2S)], crystals will form on nucleation sites (rust, scale, sand, etc.), and the mixture becomes solid. Gas molecules can occupy those spaces under the right conditions of temperature and pressure based on the solubility of the gas in water. All gases will dissolve to some degree in water at normal temperatures and under atmospheric pressure conditions.

5.0 TEMPERATURE/PRESSURE

The amount of gas that dissolves in water to occupy spaces between water molecules depends on the temperature and pressure. When pressure is high, gas compresses and fills the spaces until they are saturated. This saturation from high pressure can occur at temperatures well above the freezing point of water, which explains why hydrates occur in “warm” gas streams. Once water is saturated with gas, chemical bonds change, and crystal growth begins, leading to the eventual formation of a solid mass of water and gas called hydrates.

Each component of natural gas has a different water solubility. As a result, hydrates form at different pressures and temperatures for different compounds. Heavier gases, like pentane, are too large to occupy the spaces between the water molecules, whereas lighter gases, like methane and ethane, do so readily.

Figure 3, “Pressure-Temperature Curves for Predicting Hydrate Formation”, illustrates hydrate formation for different gas gravities. Higher gravities mean heavier gases. Heavier gases form hydrates at lower pressures than lighter gases. Also, hydrates from both light and heavy gases will form at higher pressures, even with flowing temperatures above 20C.

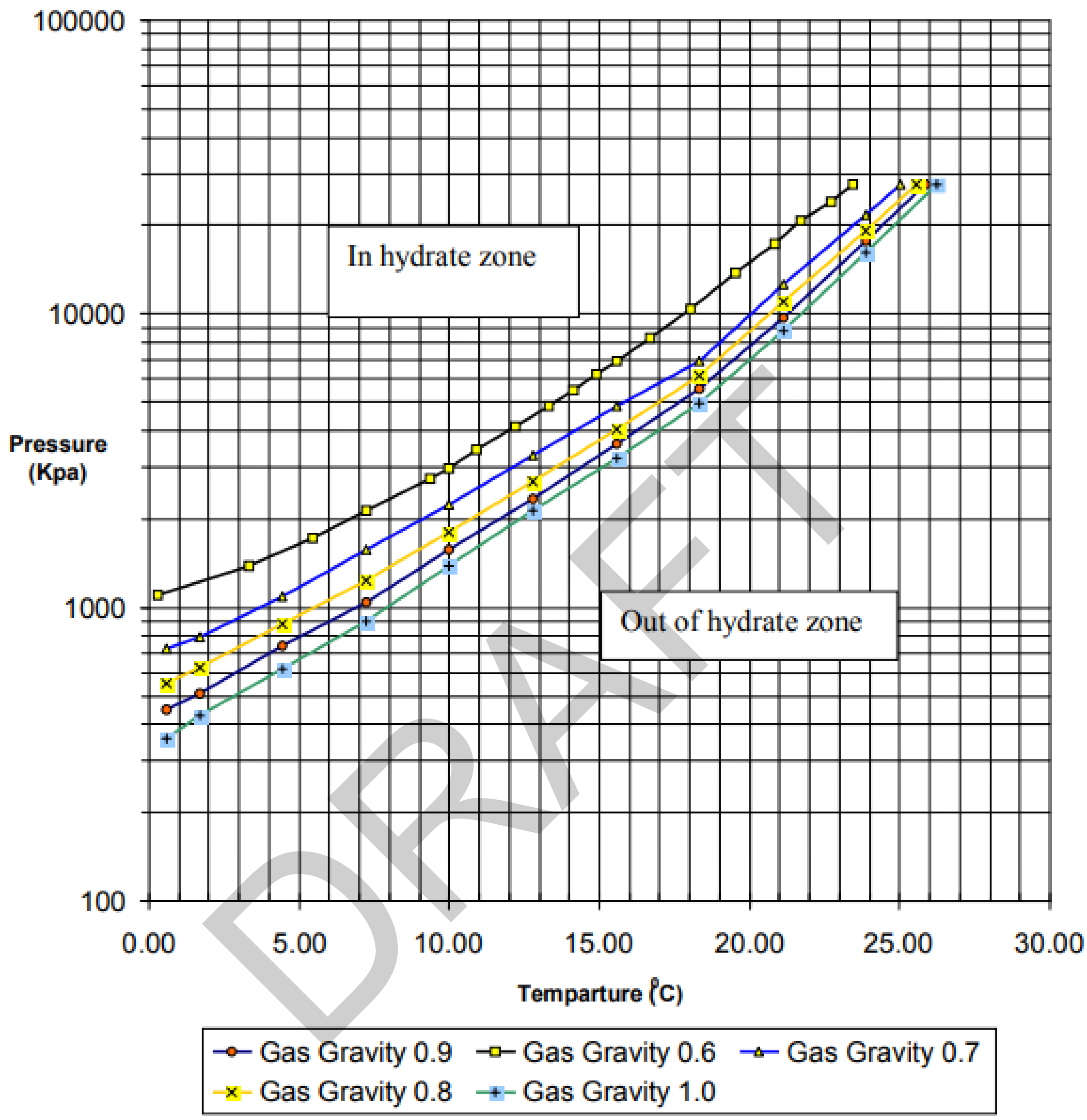

Figure 3. Pressure-Temperature Curves for Predicting Hydrate Formation (IRP #4 Well Testing and Fluid Handling)

A further complication arises if the hydrocarbon stream contains H_2S or CO_2. Then the temperature at which a hydrate could form will increase, since both gases are more soluble in water than hydrocarbon-type gases.

5.1 HYDRATES AND ICE DETECTION

Hydrates, like any other obstruction in a line, can be detected by the consequences they create. Obstructions reduce flow, increase back pressure on a system, and increase the differential pressure across the obstruction.

The exact location of the hydrate or ice plug can be determined several ways such as: based on past experience, system geometry (low spots in piping), volumetric methods (flow provers, positive displacement meters) and sonic detection methods.

Companies should develop situation-specific maximum differential pressures considering elements such as piping configuration, distance to first point of impact and public proximity. This applies to all restrictions including hydrate plugs, wax plugs and asphaltenes.

Differential pressure can quickly accelerate a moving hydrate plug to velocities approaching the speed of sound, creating excessive forces. Moving hydrates can cause serious mechanical damage at downstream locations where restrictions (control valve), obstructions (closed valve) or sharp change of direction (elbow, tee) exist.

Key Concept: It is important to first identify these potential downstream locations as the likely points of failure if an impact occurs

The failure can be either an impact or overpressure (shock wave). Keep all workers away from the potential point of impact. Impact failures occur due to the mass and momentum of the hydrate hitting and fracturing the pipe or fittings (see Figure 4 below).

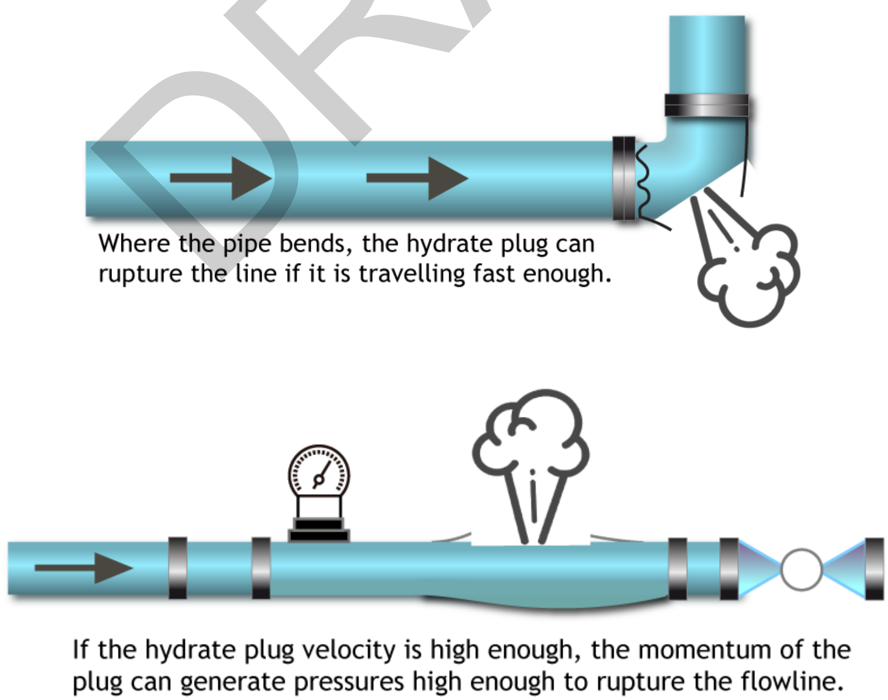

Figure 4. Impact and Overpressure Failures

5.2 HYDRATES AND ICE FORMATION

Gas hydrates form in the water phase from gas molecules dissolved in that phase. Consequently, H_2S and CO_2 increase the temperature at which hydrates will form since they are more soluble in water than most hydrocarbons. Turbulence-producing conditions (e.g., orifice meters, reduced port valves, etc.) contribute to the formation of hydrates. However, hydrates can also form under static conditions.

Hydrate formation and disintegration are not well understood. Hydrates grow like crystals, resembling wet snow in appearance. The crystallizing process is complex. Factors which contribute to the initiation of hydrate formation include:

- Degree of sub-cooling – hydrates may not begin to form immediately upon reaching the hydrate point; as much as 5C to 10C of sub-cooling is needed to form the first seed crystals of hydrates
- Presence of artificial nucleation sites – rust, scale, sand, etc.
- Degree of mixing – system geometry and flow regime

Further, once crystallization has begun, time is needed for the crystals to agglomerate (clump) and actually block the flow.

Key Concept: Hydrates take time to form and, therefore, there is time to detect them and take remedial action

Because hydrates absorb the heat as they dissociate, the system temperature can fall below the normal freezing point of water. This accounts for the confusion between hydrates and ice. Often, ice remains after hydrates have been removed.

5.3 HYDRATE AND ICE IN PIPING

Hydrate formation is a major hazard in pipelines that carry wet gas. Pockets of water will form in low points of the line and hydrates can form downstream of that water, particularly if the pipe passes through a temperature change. Apart from the pipe temperature change, the gas temperature itself will decrease while traveling through the pocket of water, resulting in a pressure drop. The saturated gas then contacts the free water at reduced temperature. For pipelines that carry wet gas and traverse changing elevations, hydrates can form at any elevation change where pockets of water lie.

Hydrates also form where there is a sharp reduction in pressure, such as at:

- Orifice plates
- Partially open control valves
- Basket strainers
- Sudden enlargement on pipelines
- Short radius elbows

The reduction in pressure causes the temperature to drop and, consequently, free water to condense.

6.0 HYDRATE AND ICE PREVENTION

Hydrates can be prevented and should not be accepted as normal operating routine. A hydrate prevention program is more effective than remedial removal measures.

The operator can prevent hydrate damage through better understanding about their formation. Hydrate formation can be prevented in any one of the following ways:

- Prevent free water in the gas stream by:
    - Dehydrating the gas, or
    - Elevating the temperature to vaporize more water
- Increase the gas temperature above the level needed for hydrate formation at the operating pressure
- Decrease the pressure below the point needed for hydrate formation at the operating temperature
- Introduce chemical inhibitors (methanol and/or glycol)
- Redesign piping system (e.g. low points, restrictions)

6.1 HYDRATE AND ICE PREVENTION EQUIPMENT

Equipment and methods used for hydrate prevention include line heaters, dehydration equipment and methanol/glycol injection systems.

Line heaters and insulated/heat traced lines keep the temperature of flowing gas above the hydrate formation temperature within a specific range of gas flow rates. This is a very effective method for hydrate prevention in steady flow conditions.

Determine safe shut-in periods for lines to avoid pressure build-up. In shut-in conditions, even insulated lines will not prevent the gas stream from cooling down to the hydrate range within hours. A safe shut-in time can be determined from temperature data gathered during short shut-in periods.

Dehydration equipment typically involves glycol dehydrators, but may also involve molecular sieve, silica gel and calcium chloride towers. Glycol dehydrators remove water vapour from the gas stream. It is important to ensure the dehydrator is working properly within its design limits.

Methanol/glycol injection systems tie up free water and water vapour to prevent hydrate formation. The choice between methanol or glycol is one of economy.

- Methanol is cheaper on a volume basis but is costly to recover and regenerate. In gas-condensate and oil streams, methanol injected is “lost” into the produced water and, to a lesser extent, in hydrocarbon liquids compared to glycol. The result is a very high injection rate compared to glycol.
- Glycol is more expensive but can be recovered and regenerated for reuse similarly to methanol. Also, glycol is comparatively more “attracted” to the water phase of the gas stream, so the injection rates are lower than methanol.

Pre-determining likely hydrate points and installing injection points or reducing hydrate possibilities by design is an effective way to engineer out potential hydrate problems. The threat of hydrates should be included in design risk assessment processes such as a Hazard and Operability Study (HAZOP) as defined by the Center for Chemical Process Safety (CCPS). In addition, supplemental glycol/methanol injection is recommended for start-ups, scheduled shutdowns and low flow conditions.

6.2 SOLUBILITY IMPLICATIONS

Glycol and methanol are water soluble and, therefore, can impact the available space between molecules to hold other compounds such as dissolved salts. As such, the use of methanol and glycol has the potential to change the solubility of these other dissolved compounds and, in certain instances, can result in increased scale formation within equipment. Therefore, the injection rates of methanol and glycol need to be selected to work in concert with scale prevention and mitigation programs.

6.3 METHANOL AND INTERNAL CORROSION

The use of methanol and glycol can impact the performance of inhibitors that are designed to coat the inside of pipes, thereby mitigating internal corrosion risk. As a result, the use of glycol and methanol to manage hydrates should be conducted in concert with the corrosion protection program to ensure that hydrate risk is managed while maintaining corrosion risk management.

6.4 CHEMICAL EXPOSURE HAZARDS

Hydrate prevention and handling may involve potential exposure to health and safety hazards associated with either process stream chemicals, such as gases and liquids (methane, H_2S, crude oil, benzene and other hydrocarbons, etc.), or chemicals used for hydrate prevention such as methanol and glycol.

For more information on controlling chemical hazards, please refer to the Controlling Chemical Hazards Guideline that was revised in 2018. Additionally ,the Fire and Explosion Hazard Management Guideline may be relevant.

7.0 HANDLING HYDRATES AND ICE

Do not attempt to remove hydrates by force through increased or decreased pressure on either side of the plug. Attempting to move hydrate plugs may rupture pipes, vessel and other equipment. The best-case scenario is to decompose the hydrate or hydrates without allowing it or them to move.

Partially hydrated systems, in which a plug is forming but has not yet completely blocked the line, can be treated with methanol or glycol once the condition that caused the hydrate is removed. If this cannot be done, shut-in and depressure the line below the hydrate formation zone as indicated in Figure 3.

The most effective way to disintegrate a hydrate that has completely blocked a line is to reduce the pressure equally on both sides of the hydrate plug. Depressuring both sides equally and at the same rate is essential to avoid movement of the partially disintegrated plug. Depressuring below the hydrate formation point will not assist disintegration and may be dangerous if the hydrate starts to move.

For piping, there may be more than one plug with full pressure trapped between them. In this situation, depressure the space between the two plugs, if possible.

Hydrates have the potential to create a line of fire hazard where workers can be in the path of potential moving objects, such as the hydrate or pressure releases. As a result, worker body positioning and other administrative controls are integral to preventing serious injuries. Additionally, equipment must be designed with line of fire hazard in mind in relation to hydrate management. This is particularly true for managing trapped pressure (stored energy) that may be located between two hydrates.

7.1 REMOVAL OPTIONS

Several removal options are presented below. These options should be considered with respect to three guiding principles:

Principle 1: Minimize the pressure differential and use hydraulics to cushion the effects of a moving hydrate. Stopping or reducing the flow will stop or limit movement of the plug.

Principle 2: Ensure that the maximum allowable working pressure (MAWP) of the system is never exceeded. Best practice is to stay below 80 percent of the MAWP.

Principle 3: Develop an emergency response plan (ERP) to handle a situation in which a pipe ruptures resulting in gas release, fire, or injury. All unnecessary personnel should be evacuated from the area and personnel should always remain out of the line of fire. Preliminary job safety procedures should be reviewed with all personnel.

The following are options for removing a hydrate plug that has completely blocked a line:

1. Disintegrate the hydrate by depressurizing equally on both sides below the hydrate point, but not to zero. Use a pressure indicator on each end of the isolation section of the line to ensure there is no significant difference in pressure (less than 10%). The pressure difference gives the plug the energy to move. Once pressure has been reduced below the point at which hydrates form, the plug will begin to disintegrate. Allow time for the hydrate to dissolve, and test for completion.

   Test for disintegration of the plug and return the line to service by the following:

   - Close the valve nearest the downstream side of the plug. The hydraulic effect of trying to move against a closed valve will have a cushioning effect.
   - Slowly pressurize the line. Both gauges should always read the same if the plug has disintegrated. If the downstream gauge does not respond at the same rate as the upstream, the plug has only partially dissolved. Depressure and allow more time.

- » Once the plug has disintegrated, ensure the condition that created the hydrate is no longer present. Slowly re-establish flow through the process. Low initial flow rates will help ensure there is not enough energy for portions of any remaining plug to cause a problem.

2. Method for longer pipelines with more than one plug.

   Isolate a section of the line, preferably at a change in elevation as this is the most likely location for a hydrate. Install a pressure indicator at each end. Slowly depressure one end of the isolation section by about 10 per cent. If both pressure indicators read the same and decrease at the same rate, the plug is not in that section. Continue to move along the pipeline and isolate the shortest possible sections, until the section containing the plug is located. Be aware that there may be more than one plug. Doing this test in the shortest possible sections reduces the distance a plug could travel once it becomes dislodged.

   - » Once located, inject methanol at one end of the line while slowly depressuring the other end. Ensure pressure does not exceed the MAWP.
   - » Do not fully depressure one side but reduce the pressure below the point of hydrate formation, close the depressuring valve and allow time for the hydrate to disintegrate. If the plug disintegrates enough to start moving, gases will start compressing against a closed valve that will slow the hydrate and minimize damage.
   - » At the injection end of the line, methanol will vaporize and move through the line by diffusion in the same way that gasoline antifreeze works in a car's gas tank.
   - » Monitor pressure indicators at each end of the line. A change in either gauge indicates a plug is moving. Stop or dramatically reduce the flow at the depressure point. Control the movement of the plug(s) by controlling the rate of depressuring. The rate of pressure decrease through the vent line will help determine the distance the hydrate is from the vent location.

8.0 RESERVOIR DEPLETION EFFECT ON HYDRATES

Maturing reservoirs frequently result in decreased flow, increasing H_2S concentrations, and increased water production and, in some segments of the system, reduced pressures. These factors can change the hydrate temperature of the system. In addition to the hydrate point, other changes from reduced volumes include reduced line velocities, increased liquid holdup, reduced heat input from the source of flow and, perhaps, line heaters in the wrong location of a heated line.

It is good practice to identify the hydrate point for each stream, so each component of the system can be operated above the temperature.

APPENDIX I – PROCESS SAFETY DATA ANALYSIS

A review and classification of available regulator reports for process safety incidents that occurred in the provinces of Alberta and British Columbia was conducted by Energy Safety Canada. Two tables from this analysis related to the prevention and management of hydrates and ice are provided below.

Table 1: Unique Incident Mechanisms

Unique Incident Mechanisms (Top Six)	Count	% of Total
Hydrate or Ice	7	14%
Reactionary Piping	3	6%
Power Failure	2	4%
Ground Disturbance	2	4%
Confined Space	2	4%
Heat	2	4%
Sub Total	**18**	**36%**

Table 2: Management System Failure Categories

Management System Failure	Primary	Secondary	Tertiary	Total	Percentage
Operation Practices & Procedures	29	13	2	44	30%
Risk Assessment	5	15	8	28	19%
Management of Change	2	5	16	23	16%
Availability of Safety Critical Devices	5	5	5	15	10%
Control of Work	0	2	11	13	9%
Inspection Program	4	4	4	12	8%
Materials of Construction	2	1	2	5	3%
Competency	1	3	0	4	3%
N/A	1	1	1	3	2%
Total	**49**	**49**	**49**	**147**	**100%**

*Competency is a subset of Operation Practices and Procedures and therefore competency is not just limited to a count of four. These four were those where the regulator specifically cited competency.

For a copy of this preliminary analysis of process safety Incidents please contact Energy Safety Canada at safety@energysafetycanada.com and request the full Process Safety Analysis presentation.

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